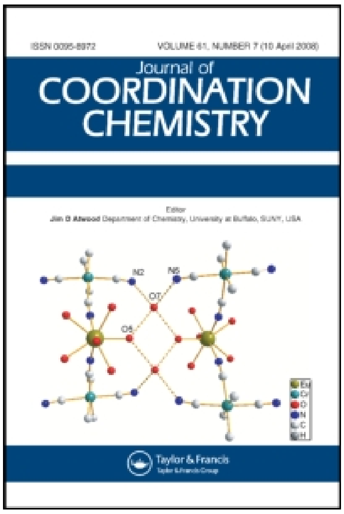

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A coordination polymer with a (3,4)-connected $(4\cdot6^2)_2(4^2\cdot6^2\cdot8^2)$ 2D network: synthesis, crystal structure and luminescent properties

Lin Xue[a]; Feng Luo[a]; Yun-xia Che[a]; Ji-min Zheng[a]
[a] Department of Chemistry, Nankai University, Tianjin, P.R. China

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A coordination polymer with a (3,4)-connected $(4 \cdot 6^2)_2(4^2 \cdot 6^2 \cdot 8^2)$ 2D network: synthesis, crystal structure and luminescent properties

LIN XUE, FENG LUO, YUN-XIA CHE and JI-MIN ZHENG*

Department of Chemistry, Nankai University, Tianjin 300071, P.R. China

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The 2D Zn(II) coordination polymer with 2,3-dicarboxypyridine acid (2,3-H_2PDC) and dimethylamine (DMA) $[Zn(2,3\text{-PDC})(DMA)]_n$ (**1**) was synthesized under solvothermal conditions and characterized by FT-IR spectroscopy, TGA and luminescent analysis. X-ray crystallographic studies of **1** reveal that this metal-organic complex has an interesting (3,4)-connected 2D network with binary nodes. The Zn ions are four-connected nodes and the 2,3-PDC ligands are three-connected nodes. Luminescent study indicates **1** has an emissive maximum at 403 nm in the solid state at room temperature.

Keywords: Solvothermal synthesis; (3,4)-Connected; 2,3-Dicarboxypyridine acid; Topology

1. Introduction

The construction of multi-dimensional metal-organic frameworks (MOFs) has been a field of rapid growth in supramolecular and materials chemistry because of the formation of fascinating structures and their potentially useful ion-exchange, adsorption, catalytic, fluorescence, and magnetic properties [1]. Analyses of network topology provide an effective way to interpret and predict MOF structures [2]. A successful strategy in building such networks is to employ the metal-ligand-directed assembly approach, which provides a way to achieve more robust polymeric structures through diverse ligands. Among the various ligands, multidentate N- or O-donors, such as pyridine or imidazole (di)carboxylic acids, have drawn extensive attention in the construction of coordination polymers or MOFs because of the diversity of the coordination modes and high structural stability [3]. In published reports, a variety of pyridine carboxylic acid coordination polymers with 3d, 4f or 3d-4f block metal ions [4] with rare and fascinating topologies are investigated, such as 3-connected 6^3 2D net [5], 4-connected $3^2 6^3$ 2D net [6], (3,4), and (3,6)-connected 3D frameworks [7].

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*Corresponding author. Email: jmzheng@public.tpt.tj.cn

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In particular, 2,3-H_2PDC is a suitable candidate, which unlike other dicarboxypyridine acids, often behaves like picolinic acid, acting as a chelating bidentate ligand through the nitrogen atom and one oxygen atom of the carboxylic group in *ortho* position; the second carboxyl group remains idle [8]. The short intramolecular distance from two adjacent carboxylate groups leads to steric torsion of the second carboxylate group vertically out of the plane, where multiple functional groups offer the potential to generate nondefault three-dimensional structures when coordinated to single metal ions [7a, 9]. In this context, we report syntheses, crystal structures and luminescent properties of a two-dimensional PDC-bridged coordination network $[Zn(2,3\text{-PDC})(DMA)]_n$ (**1**). Further topological study indicates that it exhibits a rare (3,4)-connected 2D network topology.

2. Experimental

2.1. *Reagents and physical measurements*

All reagents were bought from commercial sources without further purification. IR (KBr, pellets) spectrum was recorded in the 400–4000 cm^{-1} range using a Bio-Rad FTS 6000 infrared spectrophotometer; elemental analysis was carried out on an Elementar Vario ELIII microanalyzer. Thermogravimetric analyses were performed on a NETZSCH TG 209 thermal analyzer under flowing N_2 with a heating rate of 10°C min^{-1} between ambient temperature and 600°C. Excitation and emission spectra were obtained on a SPEX FL-2T2 spectrofluorometer equipped with a 450 W xenon lamp as the excitation source.

2.2. *Synthesis of* $[Zn(C_7H_3NO_4)(C_2H_7N)]_n$ *(1)*

Complex **1** was obtained using 2,3-dicarboxypyridine acid (0.17 g, 1 mmol), $Zn(NO_3)\cdot 6H_2O$ (0.3 g, 1 mmol), dimethylamine (0.05 g, 1 mmol) and 5 mL DMF placed in a 25 mL acid-digestion bomb at 180°C for 3 days. After cooling to room temperature (5°C h^{-1}), colorless crystals were obtained (yield 60% based on Zn. m.p. above 300°C) and then filtered off, washed with ethanol and dried in air. This complex is stable in air and insoluble in common solvents such as THF, DMF, CH_3CN, CH_3OH, C_2H_5OH, and H_2O. Elemental analysis Calcd for **1** (%): C 39.23, H 3.66, N 10.17; found: C 38.85, H 3.81, N 10.08. IR (KBr, cm^{-1}): 3279w ($\nu_{N–H}$), 3071m ($\nu_{C–H}$), 2961s ($\nu^{as}_{CH_3}$), 2806m ($\nu^{s}_{CH_3}$), 2022w ($\delta_{C–H}$), 1957w ($\delta_{C–H}$), 1781w ($\delta_{C–H}$), 1645s (ν^{as}_{COO}), 1582s (ν^{as}_{COO}), 1467s ($\delta_{C=N}$), 1402s (ν^{as}_{COO}), 1356s (ν^{as}_{COO}), 1270m $\delta_{C–N}$), 1234m, 1180w ($\delta_{C–H}$), 1155w ($\delta_{C–H}$), 1113m ($\delta_{C–H}$), 1067w ($\delta_{C–H}$), 898w, 877m, 841m, 776m, 731m, 707m, 684m (δ_{OCO}), 546m (Zn–N), 475m (Zn–O).

2.3. *X-ray crystallography*

A suitable single crystal with dimensions $0.31 \times 0.08 \times 0.07\ mm^3$ of **1** was chosen for data collection which was performed on a Rigaku R-AXIS RAPID IP diffractometer

Table 1. Crystal data and structure refinement for **1**.

Formula	($C_9H_{10}N_2O_4Zn$)
Formula weight	275.56
Crystal system	Monoclinic
Space group	$P2/c$
a (Å)	8.0900(16)
b (Å)	6.5096(13)
c (Å)	19.831(4)
β (°)	98.75(3)
V (Å^3)	1032.2(4)
Z	4
D_c (g cm^{-3})	1.773
F(000)	560
T(K)	293(2)
GOD on F^2	1.056
Final R [$I > 2\sigma(I)$]	$R_1 = 0.0598$, $wR_2 = 0.1426$
Largest diff. peak and hole (e Å^{-3})	1.218 and −0.998

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

N(1)–Zn(2)	2.039(4)	O(4)–Zn(1)	1.961(4)
N(2)–Zn(1)	2.023(5)	O(3)–Zn(2)#1	2.230(4)
O(2)–Zn(2)	2.061(3)		
O(4)#2–Zn(1)–O(4)	99.4(3)	O(2)–Zn(2)–O(2)#3	180.00(17)
O(4)–Zn(1)–N(2)#2	118.62(18)	N(1)#3–Zn(2)–O(3)#4	94.29(15)
O(4)–Zn(1)–N(2)	103.10(19)	N(1)–Zn(2)–O(3)#4	85.71(15)
N(2)#2–Zn(1)–N(2)	113.9(3)	O(2)–Zn(2)–O(3)#4	84.63(14)
N(1)#3–Zn(2)–N(1)	180.0(2)	O(2)–Zn(2)–O(3)#5	95.37(14)
N(1)#3–Zn(2)–O(2)	99.18(14)	O(3)#4–Zn(2)–O(3)#5	180.00(8)
N(1)–Zn(2)–O(2)	80.82(14)		

Symmetry code: #1: $x, y-1, z$; #2: $-x, y, -z+1/2$; #3: $-x, -y+2, -z$; #4: $x, y+1, z$; #5: $-x, -y+1, -z$.

[(Mo-Kα) = 0.71073 Å]. Cell refinement and data reduction were accomplished by the RAPID AUTO program. The structure was then solved with direct methods and refined using SHELXL-97. All non-hydrogen atoms were refined anisotropically. The N-bound H-atom was found from differential Fourier maps and treated isotropically with distance restraints, while the other H-atoms were placed in calculated positions [10]. Further details of X-ray structure analysis are given in table 1 and selected bond lengths and angles are given in table 2.

3. Results and discussion

3.1. *Description of the crystal structure of 1*

A single-crystal X-ray diffraction study reveals that **1** adopts a 2D supramolecular structure. The asymmetric unit of **1** contains two crystallographically unique

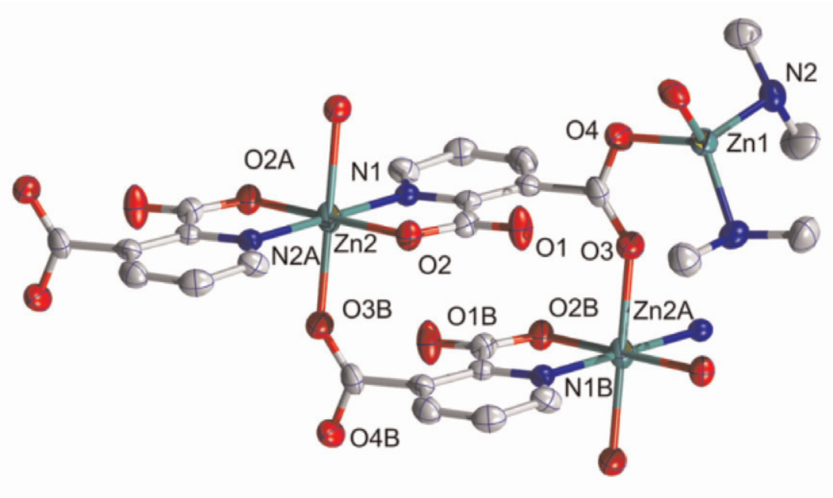

Figure 1. The thermal ellipsoid (50%) plot of **1** showing the coordination environment around the Zn ions. Hydrogen atoms were omitted for clarity.

half-occupancy Zn(II) ions, one 2,3-PDC ligand and one dimethylamine (figure 1). Zn(1) lies on a centre of symmetry and has four-coordinate tetrahedral geometry, coordinated by two N atoms from two dimethylamine molecules [Zn(1)–N(2) = 2.023(5) Å] and two *syn* 3-position carboxylate O atoms from two 2,3-PDC ligands [Zn(1)–O(4) = 1.961(4) Å]. Zn(2) also lies on a centre of symmetry and has six-coordinate distorted octahedral geometry, coordinated by N(1), N(1A), O(2), O(2A) from the two chelating 2,3-PDC ligands in the equatorial plane [Zn(2)–N(1) = 2.039(4) Å, Zn(2)–O(2) = 2.023(5) Å] and two *anti* 3-position carboxylate O atoms [Zn(2)–O(3) = 2.230(4) Å] in the axial sites. The crystallographically unique 2,3-PDC anion is tetradentate with a nitrogen, a monodentate 2-position carboxylate group connecting Zn(2), a bidentate 3-position carboxylate group bridging Zn(1) and Zn(2). As expected, the close proximal distance of two carboxylates leads to a steric torsion out of the plane of the molecule [11]. The resulting dihedral angle for the 3-position carboxylate is 87.08° when viewed down an axis from the carboxylate carbon to the adjacent pyridine core carbon. On the other hand, the 2-position carboxylate plane is essentially coplanar with the pyridyl plane (dihedral angle = 5.36°). Thus, the two types of Zn ions are intra-linked by 2,3-PDC ligands into a two-dimensional network (figure 2). When viewed along the *b*-axis, the weak C–H $\cdots$ O hydrogen bond [C(2) $\cdots$ O(1) = 3.320(6) Å] interlayer extends the structure into a three-dimensional supramolecular architecture [12] (figure 3a). Based on H-bonds, one-dimensional rectangular channels which are occupied by coordinated dimethylamine molecules can be observed (figure 3b).

From the topological point of view, the framework of **1** is a rare example of (3,4)-connected 2D network with a vertex symbol $(4 \cdot 6^2)_2(4^2 \cdot 6^2 \cdot 8^2)$ predicted by Wells [13] shown in figure 4(a). Herein, each 2,3-PDC ligand serves as a three-connected node with a short vertex symbol $(4 \cdot 6^2)$ and each Zn(2) serves as a four-connected node with a short vertex symbol $(4^2 \cdot 6^2 \cdot 8^2)$; the ratio of the number of 3-connected to

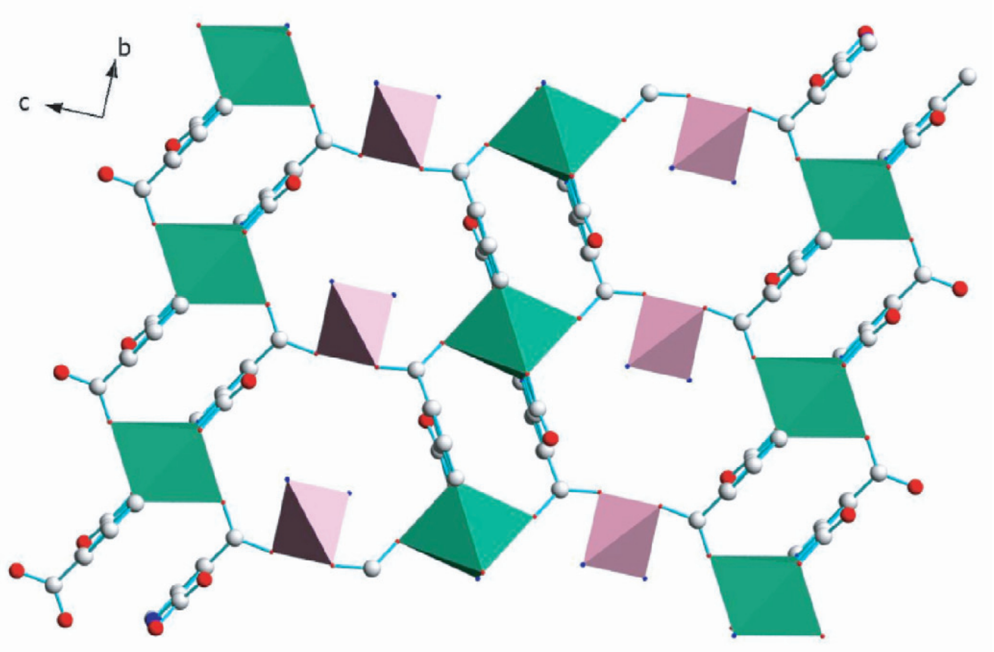

Figure 2. The 2D structure of **1** viewed along the *bc* plane. The dark green polyhedron represents a ZnN_2O_4 unit, the pink polyhedron represents a ZnN_2O_2 unit.

4-connected nodes is 2 : 1. The (3,4)-connected networks generally favor formation of 3D networks [14], and few (3,4)-connected 2D networks, $[Co_3(Hadip)_2(H_2O)_6]_n \cdot 2nH_2O]$, $[Cu_2(ip)(ipH)(4,4'\text{-bpy})_{1.5}]_n$ (H_4adip = 5-aminodiacetic-isophthalic acid, ip = isophthalate) [15], are reported. A previous 2,3-PDC-based 2D network, $[Mn_2(2,3\text{-pdc})_2(H_2O)_3]_n \cdot 2nH_2O$ [16], has similar 3-, 4-connected nodes shown in figure 4(b); it has two types of three-connected nodes, different from **1**. However, both four-connected nodes in them are almost planar to generate 2D networks.

3.2. *Ir and thermal properties of 1*

The IR spectrum gives some qualitative structural information concerning the coordination modes of the carboxylate groups. The antisymmetric and symmetric carboxyl stretching frequencies are 1645, 1582, 1402, and 1356 cm^{-1}, respectively. The two values of $\Delta(\nu_{asym} - \nu_{sym})$, 289 and 180 cm^{-1}, indicated existence of unidentate and bidentate coordinated carboxylate groups, confirmed by X-ray diffraction [17].

The thermal stability of **1** was measured by thermogravimetric analyses (TGA) on crystalline samples at 26–600°C (figure 5). The studies indicate four-step weight losses. The initial weight loss of 2.88% in the range 26–180°C corresponds to the loss of adsorbed DMF molecules. The second, third and fourth losses of 72.05% in the range 180–486°C appear to be continuous and correspond to loss of both dimethylamine and 2,3-PDC ligands (Calcd 70.5%).

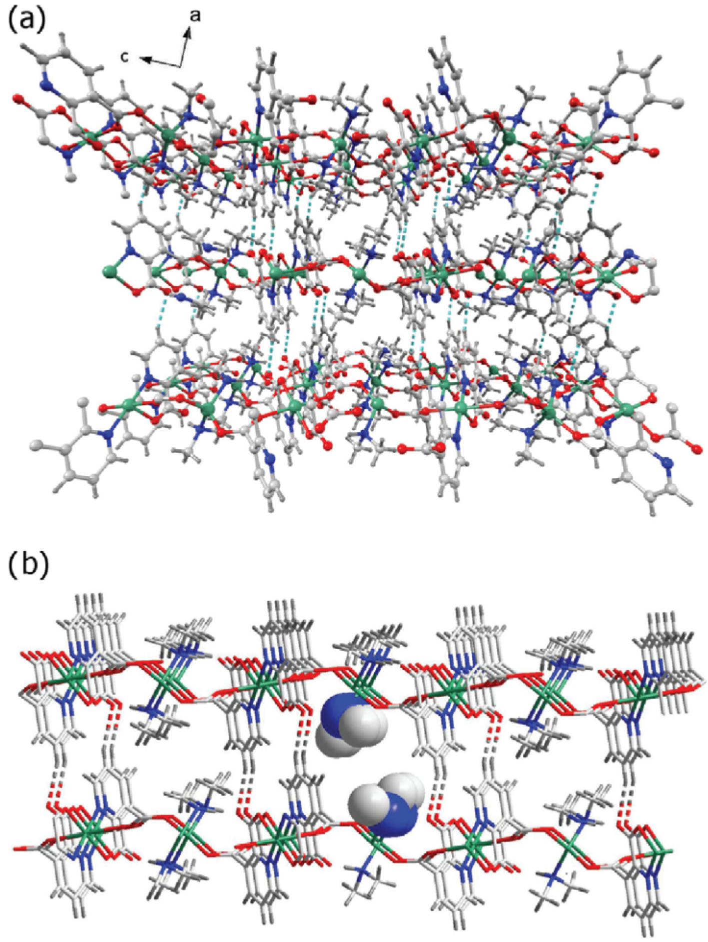

Figure 3. (a) Perspective view of the two-dimensional network of **1** viewed along the *b*-axis; (b) the one-dimensional channels occupied by coordinated dimethylamine molecules.

3.3. *Luminescent properties of 1*

The emission spectrum of **1** in the solid state at room temperature is depicted in figure 6. Intense emission occurs at 403 nm ($\lambda_{ex} = 319$ nm). We analyzed the luminescent properties of the 2,3-H_2PDC ligand and found that the emission peak for 2,3-H_2PDC is about 470 nm, attributable to the $\pi^* \rightarrow n$ transition [18]. Therefore, the emission of **1** is not related to the $\pi^* \rightarrow n$ transition of the ligand. The emission can be assigned to the ligand-to-metal charge transfer (LMCT), rather than the $\pi^* \rightarrow n$ transition of the ligand. Similar LMCT have been reported in PDC based polymers such as $[Zn_2(3,4\text{-PDC})_2(DMF)_3]_n$, $[Zn(3,4\text{-PDC})(H_2O)_2]_n$, $[Zn_2(2,3\text{-PDC})_2(H_2O)_3]_n$ and $[Zn(2,3\text{-PDC})(H_2O)_2]_n$ [8a, 19]. These observations indicate that **1** may be an excellent candidate for photoactive materials, since this condensed material is thermally stable and TGA curve shows no obvious change below 300°C.

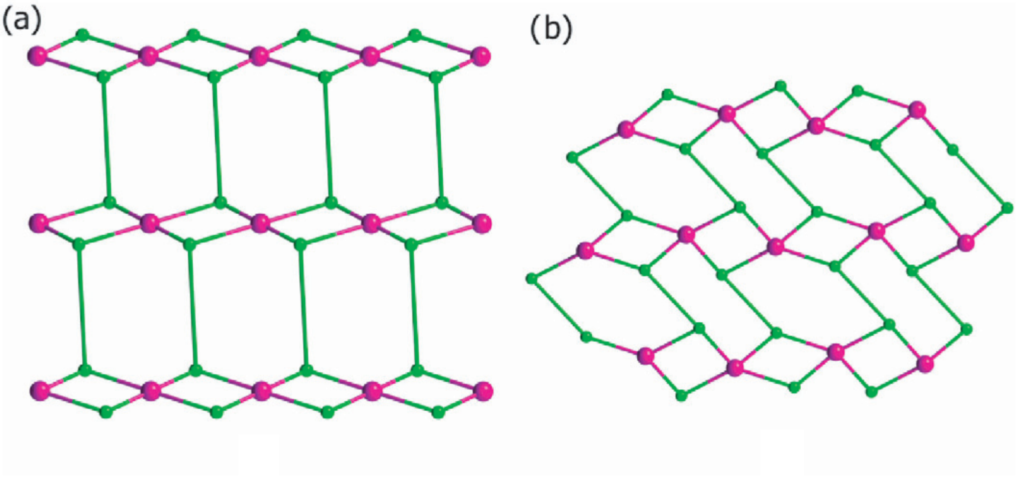

Figure 4. (a) The topological (3,4)-connected 2D network in **1**; (b) 2D network in $[Mn_2(2,3\text{-}pdc)_2(H_2O)_3]_n \cdot 2nH_2O$ [purple spheres: four-connected nodes; green spheres: three-connected nodes].

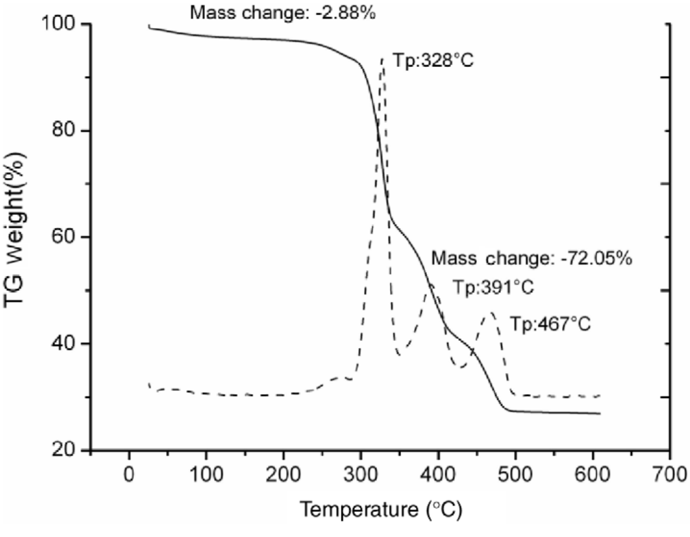

Figure 5. TGA plot of **1**.

4. Conclusion

In summary, a new 2,3-PDC-bridged complex of Zn(II) has been synthesized under solvothermal conditions. X-ray structure analysis shows all 2,3-PDC ligands are three-connected nodes and Zn(II) are four-connected nodes to generate a rare topological 2D network with vertex symbol of $(4{\cdot}6^2)_2(4^2{\cdot}6^2{\cdot}8^2)$. This work shows the capability of solvothermal synthesis for polymeric frameworks, which still remains our aim of future work.

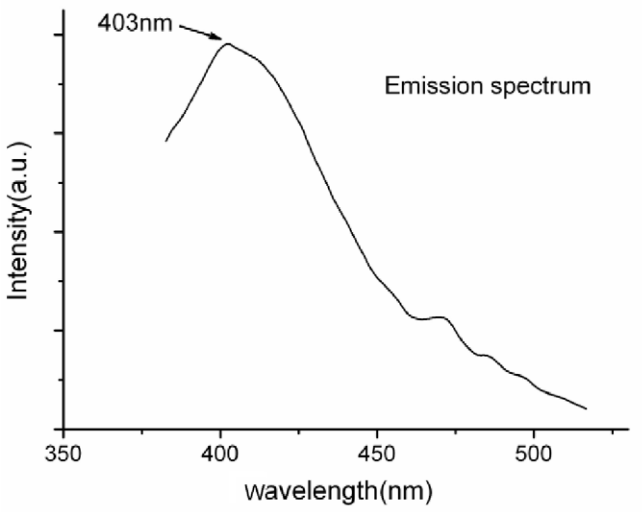

Figure 6. Solid-state emission spectrum of **1** at room temperature.

Supplementary data

CCDC No. 619655 for **1** contains the supplementary crystallographic data for this article. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk.

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